

The University of Chicago

THE PEROXIDE EFFECT
IN THE ADDITION OF REAGENTS TO
UNSATURATED COMPOUNDS

I. THE ADDITION OF HYDROGEN BROMIDE TO
TETROLIC ACID

II. THE ADDITION OF BISULFITE TO PROPYLENE

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1939

By

WLADIMIR W. GRIGORIEFF

CHICAGO, ILLINOIS

1942

The University of Chicago

THE PEROXIDE EFFECT
IN THE ADDITION OF REAGENTS TO
UNSATURATED COMPOUNDS

- I. THE ADDITION OF HYDROGEN BROMIDE TO
TETROLIC ACID
II. THE ADDITION OF BISULFITE TO PROPYLENE

A DISSERTATION SUBMITTED TO THE FACULTY OF THE
DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1939

By
WLADIMIR W. GRIGORIEFF



CHICAGO, ILLINOIS

1942

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor M. S. Kharasch for his guidance and instruction throughout this investigation and to Dr. Frank Mayo for his many helpful suggestions.

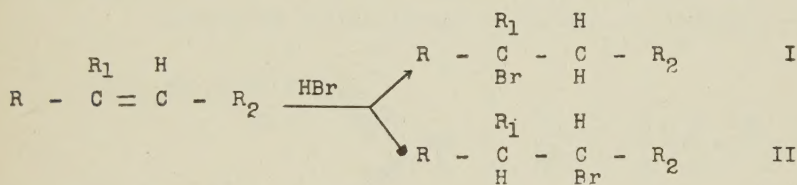


Digitized by the Internet Archive
in 2026

I. THE ADDITION OF HYDROGEN BROMIDE TO TETROLIC ACID

Introduction

The addition of hydrogen bromide to unsaturated compounds has been studied intensively in this laboratory. It has been shown that in the case of ethylene compounds two products may be obtained by addition of hydrogen bromide:



except when either R, R₁ or R₂ is a carboxyl or carbethoxy group. One of these products is usually obtained when oxygen is carefully excluded from the reaction, or if an antioxidant is used, and the other usually results when the reaction is allowed to take place in the presence of oxygen or when organic peroxide is added to the reaction mixture. These findings have been confirmed in the case of the following unsaturated compounds: propylene,¹ isobutene,² 1-butene,³ 1-pentene,⁴ allyl bromide,⁵ allyl chloride,⁶

¹Kharasch, McNab and Mayo, J. Am. Chem. Soc., 55, 2531 (1933); 56, 1425 (1934).

²Kharasch and Hinckley, ibid., 56, 1212 (1934).

³Kharasch and Hinckley, ibid., 56, 1425 (1934).

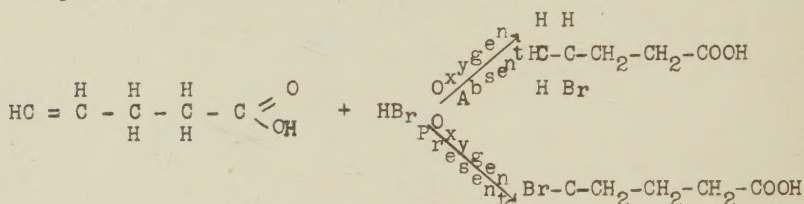
⁴Kharasch, Hinckley and Gladstone, ibid., 56, 1642 (1934).

⁵Kharasch and Mayo, ibid., 55, 2468 (1933).

⁶Shane, Ph.D. thesis, The University of Chicago.

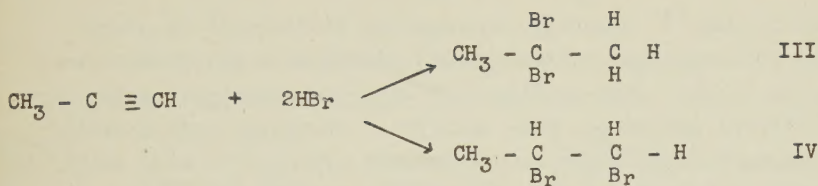
2-bromopropene,⁷ 2-chloropropene,⁷ vinyl chloride,⁸ vinyl bromide,⁹ neopentyl ethylene,¹⁰ trichloro ethylene,¹¹ styrene,¹² trimethyl ethylene.¹³

Similar observations have been made in the case of substances not containing terminal double bonds, such as trimethylene ethylene,¹³ and β -bromobutene - 2.¹⁴ However, it has been impossible to obtain more than one addition product when the double bond is next to a carboxyl group, as in acrylic or crotonic acid and their esters. If the double bond is not conjugated with the carboxyl group, the two types of addition of hydrogen bromide are readily realized. Thus allylacetic acid reacts with hydrogen bromide to yield the following compounds depending upon the presence or absence of oxygen and/or peroxides:



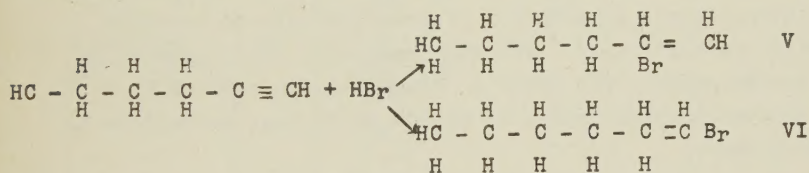
⁵ Kharasch and McNab have also shown that unsymmetrical acetylene compounds add hydrogen bromide in two different ways. Specifically, propargyl (methylacetylene) adds hydrogen bromide to yield the following compounds:

-
- ⁷ Kharasch, Engelmann and Mayo, J. Org. Chem., 2, 288 (1937).
⁸ Kharasch and Hannum, J. Am. Chem. Soc., 56, 712 (1934).
⁹ Kharasch, McNab and Mayo, ibid., 55, 2521 (1933).
¹⁰ Kharasch, Hannum and Gladstone, ibid., 56, 244 (1934).
¹¹ Kharasch, Norton and Mayo, J. Org. Chem., 3, 48 (1938).
¹² Walling, Kharasch and Mayo, unpublished work.
¹³ Walling, Kharasch and Mayo, unpublished work.
¹⁴ Walling, Kharasch and Mayo, unpublished work.
¹⁵ Kharasch and McNab, J. Am. Chem. Soc., 57, 2463 (1935).



Compound III is formed in the absence of oxygen and/or peroxide and in the presence of antioxidants, while IV is formed when the reaction is carried out in air or in the presence of an organic peroxide.

Similar observations are recorded by Young, Vogt and Nieuwland¹⁶ in the case of butylacetylene:



Here again Compound V is formed in the absence of oxygen and in the presence of antioxidants, while VI is formed in the presence of oxygen and/or peroxides.

In view of these findings it became of interest to investigate the addition of hydrogen bromide to a compound in which the triple bond is conjugated with the oxygen of a carboxyl group. Tetrollic acid was chosen for the investigation. It was also hoped that this study might help to clarify the discordant results reported by different investigators, and particularly the formation of α, β -dibromobutyric acids from the addition of hydrogen bromide to tetrollic acid.

Previous Work

Michael and Brown¹⁷ state that β -bromocrotonic acid (M.P. 95°) is formed when an aqueous solution of hydrogen bromide is added to tetrollic acid. This conclusion was confirmed

¹⁶Young, Vogt, Nieuwland, *ibid.*, 58, 55 (1936).

¹⁷Michael and Brown, *Am. Chem J.*, 9, 277 (1877).

by Clutterbuck.¹⁸ Recently, Mochnac and Stoliarov¹⁹ reinvestigated this reaction. These investigators were interested particularly in the lower melting form of β -bromocrotonic acid. Two different procedures were employed. In their first experiments an aqueous solution saturated with hydrogen bromide at 0° was added to tetrolic acid. Under these conditions, a dibromobutyric acid, which melted at 70-71°, was obtained. This acid the authors erroneously (see experimental part) assumed to be a mixture of the α, β -dibromobutyric acids. In their other experiments an aqueous solution saturated with hydrogen bromide at 25° was used. The addition reaction actually took place at 20°. The use of smaller quantities of hydrogen bromide allowed them to isolate products of addition of a single mole of hydrogen bromide to tetrolic acid. Two such compounds were isolated by these investigators, the known β -bromocrotonic acid (M.P. 95°) and a substance which melted at 79-80° which they assumed to be the cis-isomer.

Discussion of Results

The results of numerous experiments, in which hydrogen bromide was added to tetrolic acid under a variety of conditions, are summarized in Table 1 on page 5.

Figure 1 is a schematic representation of my findings of the addition of hydrogen bromide to tetrolic acid.

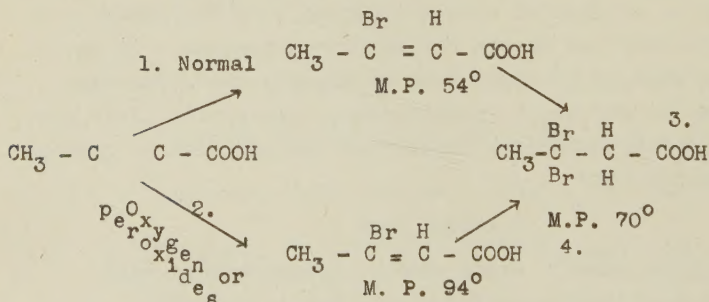


Figure 1

It can be seen at a glance that the conclusions depart in two important respects from those of previous investigators.

¹⁸Clutterbuck, Ann., 268, 108 (1892).

¹⁹Mochnac and Stoliarov, Compt. rend. Acad. Sc., U.S.S.R., 14, 559 (1937).

TABLE 1
ADDITION OF HYDROGEN BROMIDE TO TETROLIC ACID

Moles HBr	Air	Added Substances	Moles of Addendum	Products Isolated	Time in Hrs.	Temperature in °C	Remarks	
1.5	Present	Ascaridole	5%	β -bromocrotonic acid M.P. 94°	Yield 88%	100	-80°	The results were checked in Expt. #2 No % yield mentioned
1.5	Present	...	...	Tetrollic acid	100%	36	-80°	
1.5	Present	Ascaridole	5%	γ,γ -dibromobutyric acid	44%	22	+20°	
				Tetrollic acid	...			
1.3	...	...	...	Tetrollic acid	...	13	-80°	
1.2	...	Diphenylamine	5%	β -bromocrotonic acid M.P. 57°	17%	85	+20°	Yield of unreacted tetrollic is based on the total product isolated
				β,β -dibromobutyric acid	10%			
				Tetrollic acid (oil)	73%			
2.5	Present	Ascaridole	5%	β,β -dibromobutyric acid	95%	33	+20°	
2.5	Present	...	...	β,β -dibromobutyric acid	90% to 95%	24 to 72	+20°	This is a summary of 3 experiments.
3.0								
2.5	Present	Tetralin peroxide	5%	Tetrollic acid	...	33	-80°	
2.5	...	Hydroquinone	5%	β,β -dibromobutyric acid raw prod.	90% based	25	+20°	Checked in #16
3.2	...	Diphenylamine	5%	β,β -dibromobutyric acid	92%	60	+20°	Checked in #14

In the first place, the claim is made that the dibromobutyric acid is not a mixture of the α, β -dibromobutyric acid isomers, but pure β, β -dibromobutyric acid; secondly, that two different β -bromocrotonic acids result from the addition of hydrogen bromide to crotonic acid. It is most remarkable that one of these acids should be formed in the absence of oxygen and the other in the presence of peroxides.

The experimental facts which lead to the conclusion that the dibromobutyric acid (M.P. 70°) is the β, β - and not the α -isomer, are as follows: a) Under antioxidant as well as peroxide conditions the addition of two moles of hydrogen bromide to tetrolic acid yields the same compound (M.P. 70°). b) Repeated crystallizations of this acid from a variety of solvents did not effect a change in its melting point. c) Fractional sublimation of the acid in a high vacuum did not produce any separation. d) A cooling curve diagram did not indicate the presence of a mixture nor that of an unstable compound. e) A considerable depression of the melting point of this acid was observed when a mixture of known isomers of α, β -dibromobutyric acid was added to it. f) The addition of hydrogen bromide to α -bromocrotonic acid (M.P. 90°) gave the α, β -dibromobutyric acid (M.P. 87°), while the addition of hydrogen bromide to β -bromocrotonic acid (M.P. 94°) gave the β, β -acid (M.P. 70°) exclusively. g) When heated with water at 150° for twelve hours the acid (M.P. 70°) gave acetone, which was identified as the 2,4-cimtrophenylhydrazone. All of these reactions unequivocally point to the conclusion that the acid M.P. 70° , which Mochnac and Stoliarov²⁰ assumed to be the α, β -dibromobutyric acid is in reality the β, β isomer.

The conditions of addition of hydrogen bromide to tetrolic acid lead to the formation of geometric isomers providing the monobromocrotonic acid (M. P. 54°) is the β -isomer. The following experiments in my estimation offer convincing evidence that the substance M.P. 54° is the β -bromocrotonic acid, and a geometric isomer of the β -bromocrotonic acid which melts at 94° . First, the bromocrotonic acid (M.P. 54°) is a pure compound. Numerous crystallizations from different solvents did not alter the melting point of the acid. No separation was effected, either, by fractional sublimation at very

²⁰Ibid.

low pressures. Second, the addition of hydrogen bromide to the two acids (M.P. 54° and 94°) leads to the same dibromobutyric acid (M.P. 70°). The formation of β,β -dibromobutyric acid is readily understood if the two substances are geometric, and not structural, isomers.

It is assumed, therefore, that the β -bromocrotonic acid (M.P. $79-80^{\circ}$) prepared by Monchracand Stoliarov²¹ is not a pure compound but a mixture of the two stereoisomeric β -bromocrotonic acids of melting point 54° and 94° , respectively.

Isomerization of β -Bromocrotonic Acids

Numerous unsuccessful attempts were made to isomerize the β -bromocrotonic acids (M.P. 54° and 94°) into each other. Small amounts of hydrogen bromide and a peroxide, so successfully used by Kharasch, Mansfield and Mayo²² in the isomerization of cis-stilbene, had no effect on either of the β -bromocrotonic acids. This is not particularly surprising for this reagent was found by Kharasch, Mansfield and Mayo²³ to be effective in the racemization of maleic and fumaric acids and other acids. Other attempts at racemization were equally ineffective. These experiments are most important for they indicate that the mechanism of addition of hydrogen bromide to tetrolic acid is essentially different under anti-oxidant and peroxide conditions. Further work is needed to substantiate these far reaching conclusions.

Experimental

Tetrolic acid.--Tetrolic acid was prepared by the action of phosphorous pentachloride on acetoacetic ester.²⁴ The yield of tetrolic acid was improved by conducting the reaction in ligroin (B.P. 90°). This procedure is less cumbersome since smaller volumes are used. A second method of preparation was the addition

²¹Ibid.

²²Kharasch and Mansfield, J. Am. Chem. Soc., **59**, 1155 (1937).

²³Kharasch, Mansfield and Mayo, unpublished work.

²⁴Feist, Ann., **345**, 104 (1906).

of carbon dioxide to the sodium salt of propyne. The latter was prepared according to the directions of Nieuwland.²⁵ In each case the crystalline tetrolic acid was distilled at reduced pressure. The product thus obtained gave a very faint peroxide test with ammonium thiocyanate and a ferrous salt.

Technique.--The experiments in which oxygen was excluded from the reaction were performed in the following way. The tetrolic acid, with the desired amount of an antioxidant (such as hydroquinone or diphenylamine) was placed in a bomb tube, and a corresponding amount of hydrogen bromide, condensed at -80° , was placed in a second tube. These were connected by an inverted U-tube connected to the vacuum line. Both tubes were cooled by liquid nitrogen and the system evacuated to a pressure of 10^{-5} mm. of hydrogen. The yoke and the tubes were temporarily closed off from the mercury pump by means of a stop-cock, and the hydrogen bromide was allowed to warm to its boiling point, permitting the escape of dissolved gases. The tubes were again chilled in liquid nitrogen and the system evacuated. The stop-cock was closed, and the hydrogen bromide was warmed to about -70° ; it was distilled into the tube containing the tetrolic acid. The tube was chilled again, evacuated, and sealed off.

In experiments containing added peroxides, all the reactants were sealed off in one chilled tube without exclusion of air. All tubes (except when the reaction was carried out at -80° in a dewar flask) were placed in steel jackets, so that the reactions were actually carried out in the dark.

After 14 to 100 hours, the tubes were taken out of the steel jackets, chilled in a carbon dioxide acetone bath, and opened. The unreacted hydrogen bromide evaporated as the temperature of the reaction mixture reached room temperature, and the last traces were removed by connecting the tubes to a water pump.

The remaining product, usually a solid, was purified by crystallization and analyzed, as shown in Table 2.

Proof of structure of the α,β -dibromobutyric acid.--Two grams of the β,β -dibromobutyric acid, m. p. 70° , were placed in a tube, 15 cc. distilled water was added, and the tube sealed off. The reaction mixture was heated at 155° to 160° for 12 hours,

²⁵Vaughn, Hennion, Vogt and Nieuwland, J. Org. Chem, **2**, 1 (1937).

TABLE 2
ANALYSES OF THE BROMOCROTONIC ACIDS

Acid	M.P.	% Bromine		Neutralization Equivalent	
		Calcd.	Found	Calcd.	Found
β -Bromocrotonic..	94°			164	168.2
β -Bromocrotonic..	54°	43.47	43.94	164	162.7
$\beta\beta$ -Bromobutyric...	70°	65.01	64.8	122	127.4 ^a

^aThe neutralization equivalents were determined by adding an excess of sodium hydroxide solution to an aqueous solution of the sample. The mixture was allowed to stand for two hours, and the unreacted base titrated with standard sulfuric acid. In the calculations, it was assumed that one mole of sodium hydroxide was taken up by the acid, and the other mole reacted to form the unsaturated acid.

after which period the tube was cooled to -80° and opened. The liquid was fractionated and the first three cc. were collected. A solution of one gram of 2,4-dinitrophenylhydrazine dissolved in five cc. concentrated sulfuric acid and 50 cc. methyl alcohol was added to the distillate, and allowed to stand one hour at 0°. The precipitated hydrazone was collected on the filter (.5 g.). The melting point of this material was 125°-126°. Mixed with a known synthetic sample of acetone 2,4-dinitrohydrazone (M.P. 126°), the mixture showed no depression of the melting point.

Summary

1. In the presence of oxygen and ascaridole, one mole of hydrogen bromide adds to tetrolic acid to form the known β bromocrotonic acid of melting point 94°.

2. In the absence of oxygen and in the presence of an antioxidant, the addition of one mole of hydrogen bromide to tetrolic acid yields a new β -bromocrotonic acid of melting point 54°.

3. Two moles of hydrogen bromide add to tetrolic acid to give the same dibromobutyric acid irrespective of the presence

or absence of oxygen or peroxides.

4. Evidence is presented which indicates that the dibromobutyric acid (M.P. 70°) is the β,β isomer.

II. THE ADDITION OF BISULFITE TO PROPYLENE AND ETHYLENE

Introduction

Previous investigators¹ in other laboratories have reported studies of additions, and attempted additions, of bisulfite to various unsaturated compounds. The conditions and results of these studies are summarized in Table 1.

TABLE 1
PREVIOUS WORK ON THE ADDITION OF BISULFITE
TO UNSATURATED COMPOUNDS

Compound	Conditions	Result	Reference
Ethylene.....)		(Addition	lg
Cyclohexene.....)	0.25 N bisul-	(Addition	lg
Trimethylethylene..)	fite and	(Addition	lg
Pinene.....)	kieselguhr at	(Addition	lg
Dipentene.....)	25° for 10	(Addition	lg
Styrene.....)	days	(Addition	lh
Styrene.....)	25-130°; S.T. ^a	Negative ^b	la, e, f, i
Pinene.....)	25°; S.T. ^a	Negative	lf
Allyl alcohol.....)	Reflux 10-20 hrs	Addition	lb, d
Allyl alcohol.....)	100°; S.T. ^a	Allyl sulfate ^c	lc
Cinnamyl alcohol...	Reflux	Addition	le
Cinnamyl alcohol...	25°; S.T. ^a	Addition	lf
Cinnamyl alcohol...	130°; S.T. ^a	Negative	li
Limonene.....)		(Negative	lf
Geraniol.....)		(Addition	lf
Linalool.....)	25°; S.T. ^a	(Addition	lf
Rhodinol.....)		(Addition	lf
Esters and ethers)		(	
of geraniol,)		(	
linalool and cin-)		(	
namyl alcohol....)		(Negative	lf

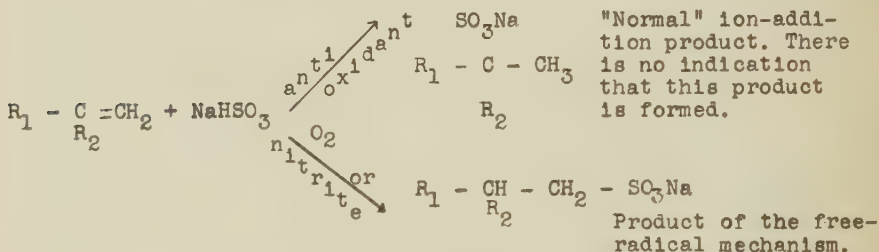
^a Sealed tube.

^b These workers obtained traces of a water-soluble organic product which was not characterized. Miller^{1a} obtained sufficient material for analysis.

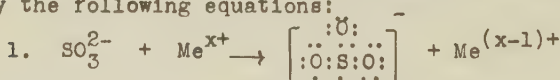
^c A possible explanation of this result is that the hydroxyl group of allyl alcohol is acted upon by bisulfite at higher temperatures. This, we believe, should be a characteristic reaction of carbinols of weakly electronegative radicals.¹ⁱ

1(a) Miller, Ann. 199, 338 (1877); (b) Mueller, Ber., 6,

It has recently been established by Kharasch, May and Mayo² that the interaction of bisulfite and ethylenic hydrocarbons proceeds only in the presence of oxygen or of suitable oxidizing agents, such as nitrite and nitrate ions. These workers found that the reactions of bisulfite with ethylene propylene, isobutylene, styrene, allyl alcohol, and cinnamyl alcohol have the characteristics to be expected of chain reactions involving a free radical mechanism. Moreover, the addition products obtained had the structures predictable for the products of a free-radical mechanism on the basis of the following scheme:



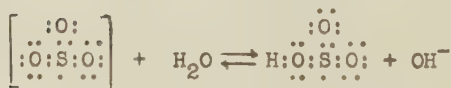
That is, hydrogen addition took place at the less electronegating of the doubly-bound carbon atoms, while the sulfonate group became attached to the more electronegative carbon atom. The addition mechanism proposed by Kharasch, May and Mayo³ is indicated by the following equations:



or



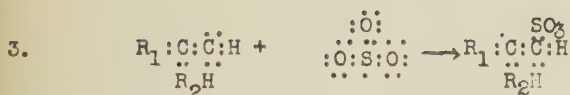
2.



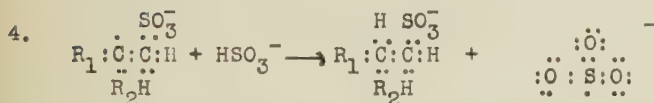
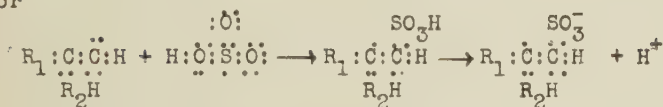
442 (1873); (c) Rosenthal, *Ann.*, 233, 38 (1886); (d) Marckwald and Frahne, *Ber.*, 31, 1864 (1898); (e) Labbe, *Bull. soc. chim.*, [3], 21, 1077 (1899); (f) DuPont, *Sci. Ind. Bull. Roure-Bertrand Fils* [3], 7, 3 (1913); (g) Kolker and Lapworth, *J. Chem. Soc.*, 1925, 307; (h) Ashworth and Burkhardt, *ibid.*, 1928, 1791; (i) Heden and Holmberg, *Chem. Zentr.*, 1937, I, 1156.

²Kharasch, May and Mayo, *J. Org. Chem.*, 3, 174 (1938).

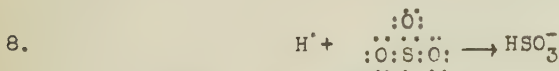
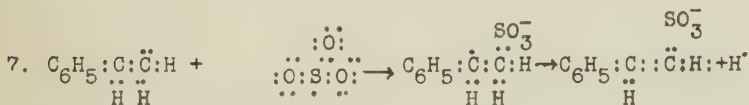
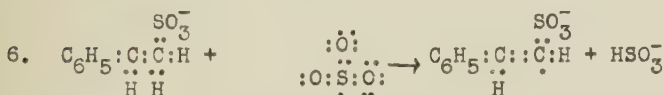
³*Ibid.*



or



The hydrogen-ion concentration of the original solution⁴ was found to have a profound effect on the rate of the reaction. It was also shown that the reaction of bisulfite with styrene yields mainly 1-phenylethylene-2-sulfonate, a substitution rather than an addition product. Kharasch, May and Mayo⁴ proposed for the substitution reaction alternative mechanisms which may be represented, respectively, by equations 5 and 6, and equations 7 and 8. Of these schemes 5 and 6 are preferable to 7 and 8.



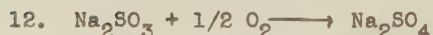
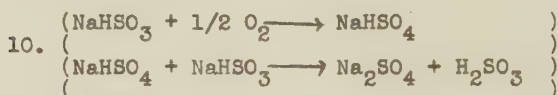
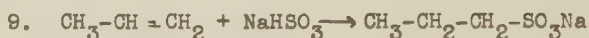
Since there is no a priori reason to believe that the proposed mechanism in 5 and 6 should be unique for styrene, the possibility that unsaturated sulfonic acids may be formed by the reaction of bisulfite with other ethylenic hydrocarbons remained to be investigated.

⁴Ibid.

Discussion of Results

In the present study, the formation of unsaturated sulfonic acids was found in the case of propylene and ethylene.⁵ The optimum pH value for the reaction of propylene with various inorganic sulfite-bisulfite mixtures, and for the reaction of ethylene with ammonium bisulfite, has been determined. The ratio of organic sulfonate to sulfate formed in the reaction with propylene is increased from .8 to 4 by the use of ethylene diamine sulfite; the oxidation of bisulfite to sulfate ions is inhibited by ethylenediamine. An interpretation of the influence of hydrogen-ion concentration on reaction rate is offered.

A clear picture of the change in hydrogen ion concentration of an aqueous solution of sodium sulfite and sodium bisulfite reacting with propylene in the presence of oxygen is revealed by examination of all the possible reactions, 9 to 12, below. For the sake of simplicity the effect on the pH of the solution of substitution reactions can be considered equal to the effect of the addition reactions.



In reaction 9 the initial pH of the sodium bisulfite solution is about 3.5; the final pH of the aqueous solution of the sodium sulfonate can be assumed to be about 7. The net effect is a tendency of the solution to become neutral, that is, more basic.

In reaction 10 the initial pH of the solution tends to diminish as the oxidation progresses; aqueous sodium bisulfite

⁵Work in progress in these laboratories has shown that hydrocarbons containing a non-terminal double bond also give unsaturated sulfonic acids.

has a smaller pH value than aqueous sodium bisulfite. The net effect is a decrease in pH of the original solution; the solution becomes less basic.

In reaction 11 the pH of the sodium sulfite solution is about 9.5; as the addition progresses, one mole of sodium hydroxide is liberated for each mole of sodium sulfite added, and the pH of the solution rises. Thus the net effect is a tendency of the solution to become more basic.

In reaction 12 the final pH of the sodium sulfate solution is about 7. The net effect is a change of pH from 9.5 to 7; the solution becomes less basic.

To summarize the oxidation of sodium bisulfite or sodium sulfite increases the acidity of the solution; the addition of bisulfite or sulfite to propylene decreases the acidity of the solution.

Preliminary work on the effect of hydrogen-ion concentration on the rate of the reaction (cf. note 2, above) showed that the rate decreases markedly at pH values greater than 6.1 and smaller than 5.1. This result was confirmed in the present investigation, and the following explanation is now offered. In acid solution there is an excess of bisulfite over sulfate ions; consequently, reaction 10 predominates, and the pH value of the solution rapidly falls to the point where reaction practically ceases. In alkaline solution, whatever addition takes place causes the liberation of a comparatively large amount of sodium hydroxide, and the solution becomes so alkaline that no further oxidation of the sulfite ion to the free radical can take place; the reaction stops.

In order to determine the conditions under which reaction proceeds readily, it is necessary to ascertain the composition of a sulfite-bisulfite solution in which the four reactions 9-12 balance each other in such a manner that the initial pH of the solution remains practically constant over the whole range of the reaction. The pH value of such a solution is here called the "optimum pH." In this study, it has been found that reaction proceeds at a maximum rate at the optimum pH, and that the ratio of sulfonate to sulfate is the greatest at this optimum pH.

Table 2 summarizes the results obtained with propylene and various mixtures of ammonium sulfite and bisulfite and sodium sulfite and bisulfite. The data recorded support the following

TABLE 2

EFFECT OF pH ON THE ADDITION OF A MIXTURE OF
SODIUM SULFITE AND SODIUM BISULFITE
TO PROPYLENE

Ex- per- iment Num- ber	Composition		Ini- tial pH	Final pH	% SO ₃ = Unre- acted	% SO ₄ = Formed	% Sul- fon- ate	% Un- satura- tion
	NaHSO ₃	Na ₂ SO ₃						
42	100%	0%	5.0	2.2	32	41	9 ^a	25.1
46	81.5%	18.5%	5.7	2.8	25	31	44	18.7
45	76.5%	23.5%	5.8	5.8 ^b	0	26	74	11.7
47	47.5%	52.5%	6.3	10.-	22	34	44	6.3
43	36.0%	64.0%	6.5	10.3	36	50	14	4.5
44	0%	100%	9.4	9.9	60	39	0	0
	(NH ₄)HSO ₃	(NH ₄) ₂ SO ₃						
53	100%	0%	5.0	2.	37	62	2	29.8
48	70.0%	30.0%	5.7	2.2	40	54	31	24.7
49	55.0%	45.0%	6.0	6.0 ^b	5	39	56	16.7
50	45.0%	55.0%	6.2	7.4	22	39	48	13.2
52	5.0%	95.0%	7.2	7.9	37	46	26	11.2
51	0%	100%	9.1	9.2	42	44	29	6.8

^aCrude sulfonate decolorizes I₂.

^bOptimum pH.

conclusions: (1) For the reaction of sodium or ammonium bisulfite or sulfite with propylene, there is an optimum pH value of the original solution; at that pH value reaction is faster than at any other. The yield of organic sulfonate is greatest at that pH, and the yield of sulfate is smallest. (2) If the pH value of the original solution is smaller than the optimum pH, the final pH value of the solution is still smaller. If the pH value of the original solution is greater than the optimum pH, the final pH value is still greater.

These statements apply to the reactions of other ethylenic hydrocarbons with sodium or ammonium sulfite-bisulfite mixtures. For example, the optimum pH value for the reaction of ethylene with ammonium sulfite-bisulfite mixtures was found to be 6.8. In all cases investigated the optimum pH for any given combination of reactants could be found by the following procedure: the final pH value of a solution is measured, and if it is higher than the original pH value, the optimum pH must be lower than the initial pH value of the solution under investigation; if the final pH value is lower than the original pH value the optimum pH must be somewhere between these two values. By taking intermediate values successively, the value of the optimum pH is obtained. If the final pH value is the same as the original one, the maximum rate is reached, and the maximum yield of sulfonate is obtained.

In an investigation of the reaction of bisulfite-sulfite mixtures with acetylene, the yields of organic sulfonate were very small. When small amounts of ethylenediamine were added, the oxidation of sulfite to sulfate was repressed, and a more rapid absorption of acetylene by the inorganic reactants was observed. Results obtained with ethylenediamine sulfite and acetylene indicated that an increase of the rate of reaction of propylene with bisulfite was to be expected; this expectation was found to be justified as is shown in Table 3. It can be concluded from the fact that the pH value rises throughout the reaction that the optimum pH lies somewhat lower than 6.9. An experiment was performed with an ethylenediamine solution brought to pH 5.97 by addition of gaseous sulfur dioxide to the aqueous solution. The final pH value of the solution was 6.63, and a 50 per cent yield of sulfate was obtained; the oxidation of the excess of sulfur dioxide by oxygen is much more rapid

TABLE 3

EFFECT OF pH ON THE ADDITION OF
ETHYLENE DIAMINE SULFITE TO PROPYLENE

Experiment No.	Composition	Initial pH	Final pH	% SO ₃ = Unre-acted	%SO ₄ ⁼ Formed	% Sul-phonate
37	"A" ^a	6.9	8.0	2	19	79
38	"A" + 1.2% "B"	7.4	8.2	2	23	75
39	"A" + 1.8% "B"	7.6	8.4	6	19	75
40	"A" + 2.4% "B"	7.7	8.5	5	22	73
41	"A" + 4.8% "B"	8.2	8.8	25	...	...
73	"A" + SO ₂	6.0	6.6	0	50	50

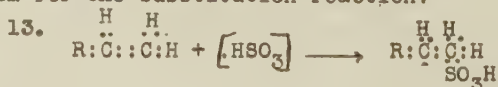
^a "A" is ethylene diamine sulfite.

"B" is ethylene diamine.

than any interaction with propylene.

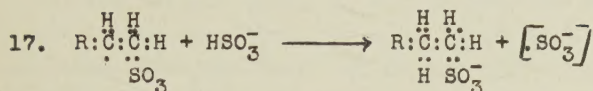
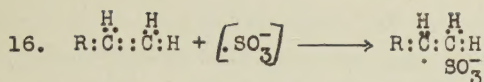
The crude organic sulfonates obtained do not reduce iodine, and therefore they are not contaminated by any sulfurous esters. A permanganate solution is decolorized by the crude organic sulfonates in the cold, a fact which indicates that an unsaturated sulfonate is present. The degree of unsaturation of the crude sulfonates was determined by a bromide-bromate titration, by the method of Lucas and Pressman,⁶ and the results obtained are tabulated in column 7 of Table 2.

The degree of unsaturation increases with decreasing pH value of the original solution, a fact which suggests following mechanism for the substitution reaction:

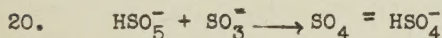
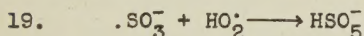
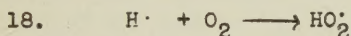


The addition reaction may be represented by the following mechanism:

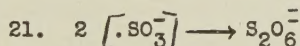
⁶Lucas and Pressman, Ind. and Eng. Chem., Anal. Ed. **10**, 140 (1938).



In the substitution reaction the bisulfite free radical is the chain-carrier; the more acid the initial solution, the more of these radicals there are in the solution, and the more substitution takes place. The hydrogen atoms formed in 14 may combine to form molecular hydrogen, or they may react with oxygen to form a radical $[\text{HO}_2\cdot]$ with branching or breaking of the chains thus:



Another reaction which leads to the breaking of the chains is the following:



This effect can easily be demonstrated by increasing the concentration of the sulfite-bisulfite mixture. A dilution factor of 4 causes a 20-fold increase of the reaction rate.

Experimental

The apparatus used was a low-pressure hydrogenator, the reservoir tank of which was filled with the olefine to a pressure of 40-45 pounds per square inch. The volume of the sulfite-bisulfite solution introduced into the pressure bottle was 50-60 cc; the volume of the bottle was 300 cc. Oxygen was bubbled at a constant rate for one minute through the solution under investigation; the pressure bottle was connected with the reservoir containing the hydrocarbon, and the connecting valve was closed. The pressure drop in the first six minutes of shaking, as detected by a guage attached to the reaction vessel, gave a qualitative test of the rate of reaction. After six minutes of shaking, the valve between the reservoir and the pressure bottle was opened,

and the shaking was continued for a specified period of time.

In the investigation of the influence of hydrogen-ion concentration on the rate of the reaction, the successive molarities of the solution, as determined by an iodine titration, were 1.40 and .02. Only one oxygen flush was used, and the total of time of shaking was an hour and a half. The original and the final pH values of the solution were measured with a glass electrode. The extent of the reaction recorded in column 4 of Table 2 was determined by an iodine titration of an aliquot part of the final solution. The reaction products were treated according to the method of Kolker and Lapworth.⁷ The mixture of barium sulfate and barium sulfite was collected on a filter, dried, and weighed. Barium sulfite was dissolved in dilute hydrochloric acid, and the remaining sulfate was weighed (column 5 of Table 2). The difference in weight between the barium sulfite and barium sulfate precipitate and the barium sulfonate provided a check on the extent of the reaction previously determined by iodine titration. The figures recorded in column 6 represent the weight of the crude sulfonate obtained, except in the case of the sodium salts, where an extraction with 85 per cent alcohol was used. In these cases the amount of sulfonate formed was found by subtracting the per cent of sulfate and the per cent of unreacted sulfite from a hundred per cent.

Summary

1. The reaction of ethylenic hydrocarbons with sulfite-bisulfite mixtures has been shown to yield saturated and unsaturated sulfonic acids.
2. The influence of the hydrogen-ion concentration on these reactions has been explained.
3. The optimum pH value for various reaction mixtures has been determined by means of a new rule.
4. A chain mechanism involving bisulfite free radicals has been proposed for the substitution reactions of ethylenic hydrocarbons with sulfite-bisulfite mixtures.

⁷Kolker and Lapworth, J. Chem. Soc., 1925, 307.

